

NASA Technical Memorandum 105220

IN-76
40043
p.11

Near-Edge Study of Gold-Substituted $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$

Mark W. Ruckman
Brookhaven National Laboratory
Upton, New York

and

Aloysius F. Hepp
Lewis Research Center
Cleveland, Ohio

(NASA-TM-105220) NEAR-EDGE STUDY OF
GOLD-SUBSTITUTED $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (NASA)
11 p CSCL 20L

N91-31977

Unclass
G3/76 0040043

September 1991

NASA



NEAR-EDGE STUDY OF GOLD-SUBSTITUTED $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$

Mark W. Ruckman
Brookhaven National Laboratory
Physics Department
Upton, New York 11973-5000

and

Aloysius F. Hepp
National Aeronautics and Space Administration
Lewis Research Center
Cleveland, Ohio 44135-3191

Abstract

The valence of Cu and Au in $\text{YBa}_2\text{Au}_{0.3}\text{Cu}_{2.7}\text{O}_{7-\delta}$ was investigated using x-ray absorption near-edge structure (XANES). X-ray and neutron diffraction studies indicate that Au goes on the Cu(1) site and Cu K-edge XANES shows that this has little effect on the oxidation state of the remaining copper. The Au L_3 edge develops a white line feature whose position lies between that of trivalent gold oxide (Au_2O_3) and monovalent potassium gold cyanide ($\text{KAu}(\text{CN})_2$) and whose height relative to the edge step is smaller than in the two reference compounds. The appearance of the Au L_3 -edge suggests that fewer Au 3d states are involved in forming the Au-O bond in $\text{YBa}_2\text{Au}_{0.3}\text{Cu}_{2.7}\text{O}_{7-\delta}$ than in trivalent gold oxide.

PACS Nos: 74.70.Vy, 78.70.Dm

Substitution of many metals in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (abbreviated as 123 in the following)¹⁻⁴ reduces the superconducting transition temperature T_c . Metals like Fe, Co, or Al replace linear chain site copper, the Cu(1) site, and depress T_c more slowly than Zn or Ni which replace copper located on the CuO_2^- planes, the Cu(2) site. X-ray absorption near-edge structure (XANES) studies^{5,6} indicate that transition metal substitutions sometimes change the oxidation state of Cu or oxygen. An apparent exception to the above generalization is the behavior of Ag and Au. Considerable amounts of Au or Ag can be put into 123 before T_c begins to decrease.⁷ Streitz et al.⁸ examined the microstructure of Au/123 composites and found that separate Au and Au-containing 123-like phases existed after heat treatment in oxygen. Hepp et al.⁹ and Cieplak et al.¹⁰ investigated $\text{YBa}_2(\text{Au}_x\text{Cu}_{1-x})_3\text{O}_{7-\delta}$ using x-ray diffraction^{9,10} and neutron scattering¹⁰ and found that Au went into the Cu(1) site.

In this communication, we report the results of an examination of the Cu K and Au L_3 x-ray absorption edges for $\text{YBa}_2(\text{Au}_x\text{Cu}_{1-x})_3\text{O}_{7-\delta}$ designed to determine the valences of Cu and Au. We find that an Au substitution of 8 mole percent has no measurable effect on the oxidation state of Cu in 123 which is divalent. The appearance of the Au L_3 edge suggests that the valence of gold is less in the superconductor than in trivalent Au_2O_3 .

Samples used in this study were synthesized and characterized at NASA Lewis Research Center; synthetic details are discussed in reference 9. For $\text{YBa}_2(\text{Au}_{0.1}\text{Cu}_{0.9})_3\text{O}_{7-\delta}$, x-ray diffraction (XRD) patterns and x-ray photoemission (XPS) suggest that "trivalent" Au goes into the Cu(1) site. When this occurs the a and b axes remain unchanged but the c axis expands from 11.69 to 11.75 Å. This is in accord with the well known

structural chemistry of Au (see reference 9 for relevant discussion). Hepp et al.⁹ found no evidence for the presence of secondary phases in their x-ray data for Au substitutions less than 10 mole percent. The formation of a second phase was readily detected in the x-ray diffraction data when more than 10 mole percent was put in 123. T_C was observed to be 89 K for the 8 mole percent gold containing material and 91 K for the parent 123 material made without Au_2O_3 . It should be emphasized at this point that the x-ray-based results of Hepp et al. have been confirmed by detailed neutron diffraction studies.¹⁰

The x-ray absorption measurements were made in the transmission mode using powdered samples dispersed on adhesive tape. Au or Cu foil absorbers were placed after the samples to run in conjunction with the samples to maintain calibrated energy scale. The work was done at the X-11A beamline at the Brookhaven National Synchrotron Light Source (NSLS). The technical details of this beamline are published in reference 11. The resolution of the monochromator is estimated to be ~ 1.0 eV at the Cu k-edge and ~ 1.2 eV at the Au L_3 edge. The samples were crushed into powder and screened through 400-mesh before dispersal onto adhesive tape. The near-edge data for the Cu K and Au L_3 edges was obtained and analyzed using standard procedures. A linear background was removed from the edge before normalization. Energy calibration of the edge was ensured by measuring the L_3 edge from a gold foil and the k-edge from a Cu foil simultaneously with the superconducting samples.

The Cu k-edges for the 123 material (solid line) and the 8 mole percent Au sample (dashed line) are shown in figure 1. The shape of the Cu k-edge is complex and several interpretations of it exist.¹²⁻¹⁶ XANES results are now available for highly oriented powders or single crystal

materials using polarized x-rays and provide the most reliable data for the Cu k edge.¹⁷⁻²⁰ The Cu k near edge structure arises from dipole transitions from the Cu 1s core level to the low-lying copper valence or conduction band states with p or π symmetry and to transitions from the Cu 1s to continuum final states that are modified by multiple scattering (shape resonances). The transitions to bound final states are related to the electron density of states and are sensitive to changes in the chemical state of the Cu while the shape resonances are sensitive to structural modification. Heald et al.¹⁷ examined the Cu k-edge from 123 powders oriented such that the x-ray polarization vector \hat{e} was either parallel or perpendicular to the c axis. The position of a weak pre-edge feature marked "A" due to 1s to 3d quadrupole transitions is marked on figure 1 and it is directly related to the valence of the Cu. In oxygen deficient 123 material, this peak grows in proportion to the removal of holes from the oxygen site and the formation of Cu¹⁺.^{21,22} Peak "B" is due to transitions from the 1s to 4p π band accompanied by shake down transitions (4p π^*) and peak "C" contains contributions from the 1s to 4p π and 1s to 4p σ transitions from the Cu(2) and the Cu(1) sites. The feature marked "D" is identified as a shape resonance. Figure 1 shows that the Cu-k edges for YBa₂Cu₃O_{7- δ} (solid line) and YBa₂(Au_{0.1}Cu_{0.9})₃O_{7- δ} (dashed line) are virtually identical which indicates that Au substitution has little or no effect on the valence of copper.

The Au L₃ edges for YBa₂(Au_{0.1}Cu_{0.9})₃O_{7- δ} , Au foil, monovalent KAu(CN)₂ and trivalent Au₂O₃ are shown in figure 2. The spectra for the reference compounds and Au substituted 123 have been normalized to the edge step of the Au absorption edge. The near-edge structure of the L₂ and L₃ edges in 5d transition metal compounds is dominated by 2p_{1/2} to 5d_{3/2}

and $2p_{3/2}$ to $5d_{1/2}$ transitions (white line feature).²³ The L_3 edge also has a contribution from the $2p_{3/2}$ to $5d_{3/2}$ level but it is much weaker than the $2p_{1/2}$ to $5d_{3/2}$ and $2p_{3/2}$ to $5d_{1/2}$ transitions. The intensity of the white line feature is thought to provide a good indication of the 5d occupation.²⁴ For Au (small dashed curve), the 5d band is filled and no white line feature is observed. The oxidation of Au to the mono or trivalent state creates the white line feature. We find that the white line area is larger for Au_2O_3 (dot-dashed line) than $KAu(CN)_2$ (dashed line) and also find that the white line feature shifts to lower photon energy when the oxidation number increases from 1+ to 3+. It should be noted that the ratio of the white line areas for Au_2O_3 and $KAu(CN)_2$ is less than the ratio of d-electron removal suggested by the valence. The white line area for Au in 123 (solid line) is considerably smaller than either of the reference compounds and lies at lower photon energy than $KAu(CN)_2$ but at a higher photon energy than Au_2O_3 .

The Au L_3 near edge data for $YBa_2(Au_{0.1}Cu_{0.9})_3O_{7-\delta}$ suggests that the valence of Au in the 123 material differs from that of Au in trivalent Au_2O_3 . Iron also replaces Cu on the chain site and is trivalent. However, the substitution of 8 mole percent Fe depresses T_C by 55 K²⁵ rather than the 2 K found for the equivalent gold substitution. Yang et al.⁵ found that Fe substitution modifies the O k-edge and reduces the number of 2p holes on the oxygen. We suggest, based on the reduction in the apparent number of unoccupied Au 5d states for the Au-O bond in 123, when compared to Au_2O_3 and the small Au-induced change in T_C , that little or no change occurs in the number of the oxygen 2p holes. This is supported by our data for the Cu k-edge which shows no change in the Cu-O bonding like that observed when the high T_C material becomes oxygen deficient and holes

are removed from the oxygen site. ²¹

The near-edge data suggests that small amounts of Au incorporated in 123 at the Cu(1) have less 5d involvement in the Au-O bond in the superconductor than in Au₂O₃. We believe this is related to the doping of the oxygen site with holes. Gold has less effect on the superconducting properties than Fe presumably because Au does not localize the holes on itself. There are no obvious changes in the Cu k-edge and we conclude that Au substitution has little or no effect on the chemical state of Cu or oxygen.

Acknowledgment

The authors thank Professor M. Croft of Rutgers University for help in obtaining some of the EXAFS data and S. M. Heald, J. Jayanetti, and E. Barrera for their help in performing and analyzing the XANES measurements. M. W. R. acknowledges the support of the U. S. Department of Energy, Division of Materials Sciences under Contract DE-AC02-CH00016. A. F. H. acknowledges support from the Space Electronics Division at NASA Lewis Research Center. The X-11 beamline and the National Synchrotron Light Source are supported by the U. S. Department of Energy under Contracts DE-AC05-80-ER10742, DE-AC02-CH00016, respectively.

References

1. J.M. Tarascon, P. Barboux, P.F. Miceli, L.H. Greene, G.M. Hull, M. Eibschutz, and S.A. Sunshine. Phys. Rev. B 36, 8393 (1987); ibid 37, 7458 (1988).
2. G. Xiao, F. H. Streitz, A. Garvin, Y. W. Du, and C. L. Chien. Phys. Rev. B 35, 8782 (1987).
3. Y. Tokura, J. B. Torrance, T. C. Huang, and A. Nazzal. Phys. Rev. B 38, 7156 (1988).
4. M. Shafer, T. Penny, B. L. Olson, R. L. Greene, and R. H. Koch. Phys. Rev. B 39, 2914 (1989).
5. C.Y. Yang, S.M. Heald, J.M. Tranquada, Y. Xu, X.L. Wang, A. R. Moodenbaugh, D. O. Welch, and M. Suenaga. Phys. Rev. B 39, 6681 (1989).
6. H. Qian, E. A. Stern, Y. Ma, R. Ingalls, M. Sarikaya, B. Thiel, R. Kurosky, C. Han, L. Hutter, and I. Aksay. Phys. Rev. B 39, 9192 (1989).
7. C. A. Chang. Appl. Phys. Lett., 52, 924 (1988).
8. F. H. Streitz, M. Z. Cieplak, G. Xiao, A. Garvin. A. Bakhshai, and C. L. Chien. Appl. Phys. Lett., 52, 91 (1988).
9. A. F. Hepp, J. R. Gaier, J. J. Pouch, and P. D. Hambourger. J. Solid State Chem., 74, 433 (1988).
10. M. Cieplak, G. Xiao, C. L. Chien, J. K. Stalick, and J. J. Rhyne. Appl. Phys. Lett. 57, 934 (1990).
11. D. E. Sayers, S. M. Heald, M. A. Pick, J. I. Budnick, E. A. Stern, and J. Wong. Nuc. Instrum. Meth., 208, 631 (1983).
12. G. Antonini, C. Calandra, F. Corni, F. C. Maticotta, and M. Sacchi. Europhys. Lett. 4, 851 (1987).

13. H. Oyanagi, H. Ihara, T. Matsubara, T. Matsushita, T. Tokumoto, M. Hirabayashi, N. Terada, K. Senzaki, Y. Kimura, and T. Yao. Jpn. J. Appl. Phys. 26, L638 (1987).
14. K. B. Garg, A. Bianconi, S. Della Longa, A. Clozza, M. De Santis and A. Marcelli. Phys. Rev. B 38, 244, (1988).
15. F.W. Lytle, R. B. Gregor, and A. J. Panson. Phys. Rev. B 37, 1550 (1988).
16. H. Tolentino, E. Dartyge, A. Fontaine, T. Gourieux, G. Krill, M. Maurer, M-F. Ravet, and G. Tourillon. Phys. Lett. A 139, 474 (1989).
17. S. M. Heald, J. M. Tranquada, A. R. Moodenbaugh, and Y. Xu. Phys. Rev. B 38, 761 (1988).
18. J. Whitmore, Y. Ma, E. A. Stern, F. C. Brown, R. L. Ingalls, J. P. Rice, B. G. Pazol, and D. M. Ginsberg. Physica B 158, 440 (1989).
19. N. Kosugi, H. Kondoh, H. Tajima, and H. Kuroda. Physica B 158, 450 (1989).
20. J. Guo, D. E. Ellis, G. L. Goodman, E. E. Alp, L. Soderholm, and G. K. Shenoy. Phys. Rev. B 41, 83 (1990).
21. J. M. Tranquada, S. M. Heald, A. R. Moodenbaugh, and Y. Xu. Phys. Rev. B 38, 8893, (1988).
22. H. Oyanagi, H. Ihara, T. Matsubara, M. Tokumoto, T. Matsushita, M. Hirabayashi, K. Murata, N. Terada, T. Yao, H. Iwasaki, and Y. Kimura. Jpn. J. Appl. Phys. 26, L1561 (1987).
23. B. Qi, I. Perez, P. H. Ansari, F. Lu, M. Croft, and D. Wieliczka. Phys. Rev. B 36, 2972 (1987).
24. I. Perez, B. Qi, G. Liang, F. Lu, M. Croft, and D. Wieliczka. Phys. Rev. B 38, 12233 (1988).
25. Y. Xu, M. Suenaga, J. Taftø, R. L. Sabatini, A. R. Moodenbaugh, and P. Zolliker. Phys. Rev. B 39, 6667 (1989).

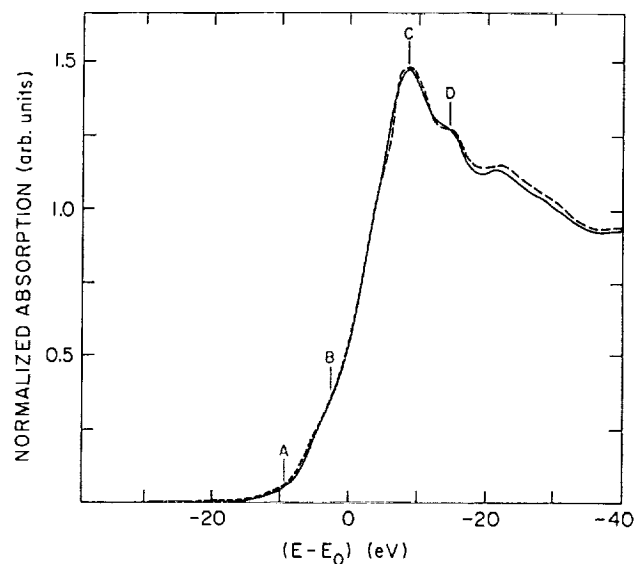


Figure 1.—Cu k-edge XANES for $\text{YBa}_2\text{Cu}_3\text{O}_{7.8}$ (solid curve) and $\text{YBa}_2\text{Au}_{0.3}\text{Au}_{2.7}\text{O}_{7.8}$ (dashed curve). The energy reference was maintained using a Cu foil.

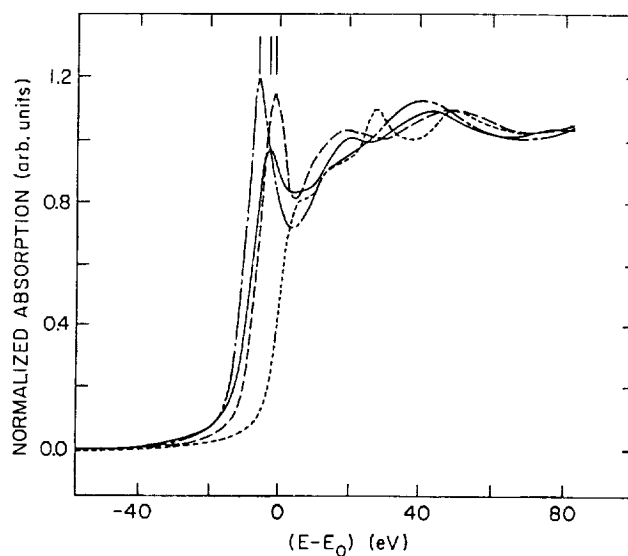


Figure 2.—Au L_3 absorption edges for gold (dotted curve), a monovalent gold compound - $\text{KAu}(\text{CN})_2$ (dashed curve), trivalent gold oxide - Au_2O_3 (dot-dashed curve) and $\text{YBa}_2\text{Au}_{0.3}\text{Au}_{2.7}\text{O}_{7.8}$ (solid). A consistent energy reference was maintained by examining the L_3 edge of a gold foil simultaneously with these samples.

REPORT DOCUMENTATION PAGE			Form Approved OMB No. 0704-0188	
Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.				
1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE September 1991		3. REPORT TYPE AND DATES COVERED Technical Memorandum
4. TITLE AND SUBTITLE Near-Edge Study of Gold-Substituted $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$			5. FUNDING NUMBERS WU-506-41-11	
6. AUTHOR(S) Mark W. Ruckman and Aloysius F. Hepp				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) National Aeronautics and Space Administration Lewis Research Center Cleveland, Ohio 44135-3191			8. PERFORMING ORGANIZATION REPORT NUMBER E-6509	
9. SPONSORING/MONITORING AGENCY NAMES(S) AND ADDRESS(ES) National Aeronautics and Space Administration Washington, D.C. 20546-0001			10. SPONSORING/MONITORING AGENCY REPORT NUMBER NASA TM-105220	
11. SUPPLEMENTARY NOTES Mark W. Ruckman, Brookhaven National Laboratory, Physics Department, Upton, New York 11973-5000; Aloysius F. Hepp, NASA Lewis Research Center. Responsible person, Aloysius F. Hepp, (216) 433-3835.				
12a. DISTRIBUTION/AVAILABILITY STATEMENT Unclassified - Unlimited Subject Categories 25 and 76			12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) The valence of Cu and Au in $\text{YBa}_2\text{Au}_{0.3}\text{Cu}_{2.7}\text{O}_{7-\delta}$ was investigated using x-ray absorption near-edge structure (XANES). X-ray and neutron diffraction studies indicate that Au goes on the Cu(1) site and Cu K-edge XANES shows that this has little effect on the oxidation state of the remaining copper. The Au L_3 edge develops a white line feature whose position lies between that of trivalent gold oxide (Au_2O_3) and monovalent potassium gold cyanide ($\text{KAu}(\text{CN})_2$) and whose height relative to the edge step is smaller than in the two reference compounds. The appearance of the Au L_3 -edge suggests that fewer Au 3d states are involved in forming the Au-O bond in $\text{YBa}_2\text{Au}_{0.3}\text{Cu}_{2.7}\text{O}_{7-\delta}$ than in trivalent gold oxide.				
14. SUBJECT TERMS Gold-substituted $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$; XANES; Valence of gold; Copper			15. NUMBER OF PAGES 10	
			16. PRICE CODE A02	
17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF ABSTRACT	